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(54) Catalyst for di-, oligo-, co- and
poly- merization of vinyl monomers

(57) A catalyst for di-, oligo-, co- and
poly- merization of vinyl monomers
comprises a compound of a transition
metal of Group IV or V of the periodic
system deposited onto a polymeric car-
rier which is a macroporous copolymer
of a vinyl and a divinyl monomer with a
specific surface area of 30 to 700 m²/g,
and a co-catalyst which is an organo-
aluminium compound.

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SPECIFICATION

Catalyst for di-, oligo-, co- and poly-merization of vinyl monomers

5 This invention relates to a catalyst for di-, oligo-, co- and poly-merization of vinyl monomers which is useful in the production of polymers.

The present invention provides a catalyst for di-,
10 oligo-, co-, and poly-merization of vinyl monomers, comprising an active phase which is a compound of a transition metal of Group IV or V of the periodic system deposited onto a polymeric carrier comprising a macroporous copolymer of vinyl and divinyl
15 monomers with a specific surface area of from 30 to 700 m²/g, and a cocatalyst which is an organo-aluminium compound.

The term "macroporous copolymer" as used herein means a two-phase system, wherein the
20 polymeric compound is pierced with communication cavities (pores) capable of being filled with an external medium upon submersion therein.

The use in the catalyst according to the invention of a carrier with a specific surface area of below 30
25 m²/g is inexpedient due to the low activity of the catalyst. The use in the catalyst of a carrier with a specific surface area of above 700 m²/g is hindered due to technological difficulties of production of such a carrier.

30 It is preferable that the catalyst contain a carrier with a pore volume of from 0.3 to 2.8 cm³/g. The use of a carrier with a pore volume of below 0.3 cm³/g is inefficient, since the carrier would have a small capacity with respect to the active phase, whereas
35 the use of a carrier with a pore volume above 2.8 cm³/g is hindered due to the high brittleness of such a carrier.

It is preferable that the catalyst contains as the carrier, a copolymer of styrene and divinylbenzene, a
40 copolymer of styrene and diisopropenylbenzene, a copolymer of styrene, divinylbenzene and methylmethacrylate, or a copolymer of styrene, ethyldivinylbenzene and vinylpyridine.

The use, as the carrier, of one of the above-mentioned copolymers of vinyl and divinyl monomers makes it possible to substantially increase the
45 specific activity of the catalyst.

It is preferable that the catalyst has a particle size of from 0.001 to 1 mm. The use of a catalyst with the
50 particle size of from 0.001 to 1 mm makes it possible to control the particle size and distribution with respect to the size of the resulting polymer particles.

It is preferable if the catalyst is in a granulated form. The control of the shape of the catalyst
55 particles makes it possible to obtain, during synthesis, polymeric particles of a shape which ensures the most favourable hydrodynamic conditions in the reactor.

The catalyst should preferably contain, as the
60 active phase, a compound of titanium or vanadium, more preferably in the form of chlorides thereof.

The catalyst should preferably contain 1 to 60% by weight of the active phase thereof. If the content of the active phase is below 1% by weight the catalyst
65 has a low activity, while if the content of the active

phase exceeds 60% by weight the catalyst activity per unit mass of the transition metal is lowered (i.e. the specific activity of the catalyst is reduced).

The catalyst according to the invention is preferably prepared in the following manner.

The macroporous carrier is a macroporous copolymer of monovinyl monomers such as styrene, ethylstyrene, diethylstyrene, isopropylstyrene, methylacrylate and methylmethacrylate with divinyl
75 monomers such as divinylbenzene, ethyldivinylbenzene and diisopropenylbenzene. Such copolymers are produced by radical-type copolymerization in the presence of a pore-forming agent. The specific surface area (m²/g) and total pore volume (cm³/g) of the resulting macroporous copolymers slightly depend on the composition of the monomeric mixture and are defined by the amount and nature of the pore-forming agent.

The pore-forming agent is a low- or high-molecular weight compound easily soluble in the monomer mixture, non-copolymerizable, and readily-removable from the resulting copolymer.

The amount of the transition metal deposited onto the surface of the polymeric carrier may be varied
90 within any desired range.

To obtain a catalyst based on titanium chloride, the carrier is treated with titanium chloride or a solution thereof under vacuum or in an atmosphere of an inert gas at a temperature of from -70 to
95 +180°C.

It is possible to prepare a catalyst based on titanium chloride by way of treatment of the carrier in succession or in combination with titanium chloride and an organo-aluminium compound (or with
100 solutions thereof) under vacuum or in an atmosphere of an inert gas at a temperature of from -70 to 180°C. The resulting catalyst is dried under vacuum at a temperature of 80 to 180°C.

To prepare a catalyst based on vanadium chloride, the carrier is treated with vapours or solutions of vanadium chloride and dried under vacuum.

A high activity of the catalyst is obtained by using, as the carrier, a macroporous copolymer with a specific surface area of from 30 to 700 m²/g. The use
110 of a carrier with a high specific surface area makes it possible to obtain a catalyst with a finely-dispersed crystalline phase of titanium or vanadium chloride. This brings about a higher efficiency of the compound of the transition metal and also an increased activity of the catalyst.

The use of macroporous polymeric carriers makes it possible to produce catalysts with a high content of a salt of titanium or vanadium. Macroporosity increases the capacity of the carrier with respect to chlorides of vanadium or titanium.

The use of a carrier as described above enables the production of a highly-active catalyst with the surface of the carrier being accessible for a monomer and coated with a salt of the transition metal.

The catalysts according to the present invention are employed in processes of dimerization, oligomerization, copolymerization and polymerization of vinyl monomers. These processes occur under an increased pressure and under vacuum, at concentrations of the monomer of from 0.01 to 100% by
130

weight, and at a temperature of from 70 to 180°C.

Owing to the use of the catalysts according to the present invention these processes proceed with a higher yield of dimers, oligomers and (co)polymers, and at a low degree of contamination thereof with inorganic residues which permits the use of the polymeric products without any additional washing.

Another advantage of the present invention is that the granulometric composition of a polymer resulting from a synthesis may be controlled by adjusting the granulometric composition of the catalyst.

The particle size of the polymer depends on the yield of the polymer per unit weight of the catalyst and on the particle size of the carrier. The yield of the polymer, in turn, is defined by the activity of the catalyst, the concentration of the monomer and the duration of the polymerization.

Under identical polymerization conditions, the polymer particle size is defined by the particle size of the carrier.

The invention will be further described with reference to the following illustrative Examples. In Examples 1 to 27 the particle size of the catalyst is determined by the particle size of the carrier.

Example 1

Preparation of the catalyst

1.18 g of a carrier with a particle size of from 0.3 to 0.8 mm in the form of spherical granules comprising a copolymer of styrene (70% by weight) with divinylbenzene (30% by weight) with a specific surface area of 160 m²/g and a pore volume of 1.65 g/cm³ were placed in a dry flask. The flask with the carrier was set under vacuum and the carrier was treated with vapours of titanium chloride in an amount of 0.15 g and cooled. Then the carrier was treated with vapours of diethylaluminium chloride in an amount of 0.065 g. The resulting catalyst was heated to a temperature of 180°C for 3 hours under vacuum. Analysis showed that the content of titanium chloride in the thus-prepared catalyst was 1% by weight and that of the carrier was 99% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

0.15 g of the catalyst, 1.1 g of diethylaluminium chloride, 5.7×10^{-3} mole of hydrogen and 130 g of propylene were charged into an autoclave with a stirrer and having a capacity of 300 ml. Polymerization was conducted at a temperature of 60°C under a pressure of 60 atm.g. After 5.5 hours there were obtained 16.9 g of polypropylene with a particle size of 1.5-4 mm in the form of spherical granules. The content of the fraction insoluble in boiling n-heptane was 86% by weight. The yield of the polymer per one gram of titanium was 36.14 kg, and the ash content was 0.0046% by weight.

Example 2

Polymerization of propylene

0.08 g of a catalyst prepared in a manner similar to that described in the foregoing Example 1, with a particle size of from 0.1 to 0.25 mm, 0.76 g of diethylaluminium chloride, 5.7×10^{-3} mole of hydrogen and 130 g of propylene were charged into an

autoclave with a capacity of 300 ml and provided with a stirrer. Polymerization was conducted at a temperature of 60°C under a pressure of 60 atm.g. After 5 hours there were obtained 8 g of polypropylene with a particle size of from 0.5 to 1.4 mm in the form of spherical granules. The yield of the polymer per one gram of titanium was 32 kg, and the ash content was 0.0052% by weight. The molecular weight of the thus-prepared polypropylene was 1.5×10^6 .

Example 3

Preparation of the catalyst

5 g of a carrier with a particle size of from 0.5 to 0.9 mm in the form of spherical granules comprising a copolymer of 60% by weight of styrene and 40% by weight of divinyl benzene with a specific surface area of 274 m²/g and a pore volume of 1.56 cm³/g were placed into a dry flask. The flask with the carrier was set under vacuum, and the carrier was treated with vapours of titanium chloride in an amount of 0.52 g and cooled. Then the carrier was treated with vapours of diethylaluminium chloride in an amount of 0.162 g. The catalyst was heated at a temperature of 180°C for 3 hours under vacuum. Analysis showed that the content of titanium chloride in the resulting catalyst was 1% by weight and that of the carrier was 99% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

0.1 g of the catalyst, 1 g of diethylaluminium chloride and 130 g of propylene were placed in a 300 ml autoclave. Polymerization of propylene was conducted at a temperature of 70°C under a pressure of 60 atm.g. After 6.6 hours there were obtained 12.8 g of polypropylene with a particle size of from 2.7 to 5.0 mm in the form of spherical granules. The density of the resulting polymeric particles was 0.87 to 0.92 g/cm³. The yield of polypropylene was 41.1 kg per one gram of titanium, and the ash content was 0.011% by weight.

Example 4

Polymerization of propylene

0.0558 g of the catalyst prepared in Example 3, with a particle size of from 0.25 to 0.5 mm, 0.3093 g of diethylaluminium chloride and 130 g of propylene were placed in a 300 ml autoclave. Polymerization was conducted at a temperature of 70°C under a pressure of 60 atm.g. After 7 hours there were obtained 7.3 g of polypropylene with a particle size of from 1.5 to 2.8 mm in the form of spherical granules. The yield of polypropylene per one gram of titanium was 41.5 kg, and the ash content was 0.0108% by weight.

Example 5

Preparation of the catalyst

0.1412 g of titanium chloride and 0.0599 g of diethylaluminium chloride were mixed in a 100 ml flask under a pressure of 10^{-2} mm Hg and at a temperature of -30°C. To the resulting mixture was added 1.08 g of a carrier with a particle size of from 0.03 to 1 mm in the form of spherical granules and

comprising a copolymer of 60% by weight styrene and 40% by weight of divinylbenzene with a specific surface area of 360 m²/g and a pore volume of 1.42 cm³/g. The flask contents were maintained under vacuum at a temperature of -10°C. The resulting catalyst was maintained at a temperature of 80°C for 10 hours under vacuum. Analysis showed that the content of titanium chloride in the catalyst was 1% by weight and that of the carrier was 99% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

0.12 g of the catalyst, 0.3 g of diethylaluminium chloride, 5.7×10^{-3} mole of hydrogen and 130 g of propylene were charged into an autoclave provided with a stirrer. Polymerization was conducted at a temperature of 60°C under a pressure of 60 atm.g. After 16.5 hours there were obtained 27 g of polypropylene with a particle size of from 0.2 to 0.7 mm in the form of spherical granules. The yield of polypropylene was 72.2 kg per one gram of titanium, and the ash content was 0.0023% by weight.

Example 6

Preparation of the catalyst

0.3094 g of a carrier with a particle size of from 0.03 to 0.1 mm in the form of spherical granules and comprising a copolymer of 85% by weight of styrene and 15% by weight of divinylbenzene with a specific surface area of 97 m²/g and a pore volume of 1.25 cm³/g were placed in a flask. The flask with the carrier was set under vacuum and the carrier was successively treated with vapours of titanium chloride in an amount of 0.0687 g and diethylaluminium chloride in an amount of 0.0206 g as described in the foregoing Example 1. Analysis showed that the catalyst contained 3% by weight of titanium chloride and 97% by weight of the carrier. The catalyst had the form of spherical granules.

Polymerization of propylene

0.1 g of the catalyst, 0.836 g of diethylaluminium chloride and 130 g of propylene were charged into an autoclave with a capacity of 300 ml and provided with a stirrer. Polymerization was conducted at a temperature of 70°C and under a pressure of 60 atm.g. After 5.9 hours there were obtained 7.8 g of polypropylene in the form of spherical particles with a size of from 0.15 to 0.45 mm. The yield of polypropylene was 8.35 kg per one gram of titanium, and the ash content was 0.029% by weight.

Example 7

Preparation of the catalyst

0.3301 g of a carrier with a particle size of from 0.25 to 0.4 mm in the form of spherical granules and comprising a copolymer of 88% by weight of styrene and 12% by weight of diisopropenylbenzene with a specific surface area of 60 m²/g and a pore volume of 1.0 cm³/g were treated with a mixture of 0.2545 g of titanium chloride and 0.0824 g diethylaluminium chloride under vacuum as described in the foregoing Example 1. Analysis showed that the catalyst contained 9.82% by weight of titanium chloride and 90.18% by weight of the carrier. The catalyst was in

the form of spherical granules.

Polymerization of propylene

0.17 g of the catalyst, 0.3 g of diethylaluminium chloride and 130 g of propylene were charged into an autoclave provided with a stirrer. Polymerization was conducted at a temperature of 70°C under a pressure of 60 atm.g. After 5.85 hours there were obtained 29.5 g of polypropylene with a particle size of from 1.5 to 2.4 mm in the form of spherical granules. The yield of polypropylene was 5.72 kg per one gram of titanium, and the ash content was 0.08% by weight.

Example 8

Polymerization of ethylene

0.1 g of the catalyst prepared as in the foregoing Example 7, with a particle size of from 0.25 to 0.4 mm, 1g of diethylaluminium chloride and 110 ml of toluene were placed in the reactor and ethylene was admitted thereto. Polymerization was conducted at a temperature of 60°C under a constant pressure of ethylene equal to 0.5 atm.g. After 8.5 hours there were obtained 7 g of polyethylene with a particle size of from 1 to 2.0 mm in the form of spherical granules. The rate of polymerization of ethylene was 530 g of polyethylene/g of titanium.hr.atm.

Example 9

Preparation of the catalyst

0.746 g of a carrier in the form of spherical granules and comprising a copolymer of 60% by weight of styrene with 30% by weight of divinylbenzene and 10% by weight of methylmethacrylate with a specific surface area of 134 m²/g and a pore volume of 1.34 cm³/g were treated with vapours of titanium chloride in an amount of 0.0971 g and maintained for 5 hours at a temperature 80°C. Analysis showed that the catalyst contained 5.6% by weight of titanium chloride and 94.4% by weight of the carrier. The catalyst was in the form of spherical granules.

Oligomerization of propylene

0.095 g of the catalyst, 0.94 g of diethylaluminium chloride and 130 g of propylene were charged into an autoclave provided with a stirrer. Oligomerization was conducted at a temperature of 70°C under a pressure of 60 atm.g. After 6.4 hours there were obtained 11.9 g of liquid oligomers. The yield of oligomers of propylene was 9.1 kg per one gram of titanium. The molecular weight of the resulting oligomers was about 150.

Example 10

Dimerization of ethylene

0.007 of a catalyst similar to that obtained in Example 9, 1.08 g of ethylaluminium dichloride and 0.2 litres of benzene were charged into an autoclave provided with a stirrer and ethylene was admitted thereto. Dimerization was effected at a temperature of 20°C under a pressure of 25 atm.g. for 2 hours. During the dimerization the pressure of ethylene was maintained constant. The yield of butenes was 94% by weight. The yield of butenes per

one gram of titanium was 6,100 kg.

Example 11

Preparation of the catalyst

- 5 0.26 g of a carrier with a particle size of from 0.25 to 0.5 mm in the form of spherical granules and comprising a copolymer of 60% by weight of styrene and 40% by weight of divinylbenzene with a specific surface area of 260 m²/g and a pore volume of 1.5 cm³/g was maintained under vacuum for 4 hours at a temperature of 80°C, cooled to room temperature and treated with vapours of vanadium chloride in an amount of 0.153 g. Analysis showed that the content of vanadium chloride was 32% by weight and that of the carrier was 68% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

- 20 0.045 g of the catalyst, 0.04 g of Al(i-C₄H₉)₃ and 50 ml of n-heptane were charged into a reactor provided with a stirrer. At a temperature of 60°C propylene was admitted into the reactor and polymerization was conducted under a constant pressure of propylene of 470 mm Hg. Within 2 hours there were obtained 1.32 g of polypropylene with a particle size of 2-3 mm in the form of spherical granules. The rate of polymerization was 240 g/g titanium.hr.atm. The content of a fraction insoluble in n-heptane was 83% by weight. The density of particles was as high as 0.9 g/cm³. The molecular weight of the polymer was about 10⁶.

Example 12

Polymerization of propylene

- 35 0.067 g of a catalyst similar to that produced in Example 11, with a particle size of from 0.001 to 0.03 mm, 0.06 g of triisobutylaluminium and 70 ml of n-heptane were charged into a reactor provided with a stirrer. At a temperature of 60°C propylene was admitted thereto and polymerization was conducted under a constant pressure of the monomer of 470 mm Hg. After 2 hours there were obtained 2.4 g of polypropylene in the form of a powder with a particle size of from 0.2 to 0.4 mm. The yield of polypropylene was 0.334 kg per one gram of vanadium. The rate of polymerization was 270 g/g of vanadium.hr.atm.

Example 13

Preparation of the catalyst

- 50 0.187 g of a carrier with a particle size of from 0.25 to 0.5 mm in the form of spherical granules and comprising a copolymer of 60% by weight of styrene and 40% by weight of divinylbenzene with a specific surface area of 260 m²/g and a pore volume of 1.5 cm³/g was prepared as described in Example 11 and treated with vapours of vanadium chloride in an amount of 0.35 g. The resulting catalyst was dried under vacuum at a temperature of 80°C. Analysis showed that the content of vanadium chloride was 60% by weight and that of the carrier was 40% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

- 0.0873 g of the catalyst, 0.0927 g of Al(i-C₄H₉)₃ and 70 ml of n-heptane were charged into a reactor provided with a stirrer. At a temperature of 60°C propylene was admitted thereto and polymerization was effected under a constant pressure of the monomer of 470 mm Hg. After two hours there were obtained 3.7 g of a polymer with a particle size of 2-3 mm in the form of spherical granules. The yield of polypropylene was 0.216 kg per one gram of vanadium. The rate of polymerization was 175 g/g vanadium.hr.atm.

Example 14

Polymerization of ethylene

- 80 0.046 g of a catalyst similar to that produced in Example 11, with a particle size of from 0.001 to 0.03 mm, 0.025 g of triisobutylaluminium and 50 ml of n-heptane were charged into a reactor provided with a stirrer. At a temperature of 80°C ethylene was admitted thereto and polymerization was carried out under a constant pressure of the monomer of 223 mm Hg. After 3 hours there were obtained 11.1 g of polyethylene in the form of a powder with a particle size of from 0.2 to 0.5 mm. The yield of polyethylene was 2.38 kg per one gram of vanadium. The rate of polymerization was 2,700 g/g vanadium.hr.atm.

Example 15

Preparation of the catalyst

- 95 0.903 g of a carrier with a particle size of from 0.25 to 0.5 mm in the form of spherical granules and comprising a copolymer of 60% by weight of styrene and 40% by weight of divinylbenzene with a specific surface area of 260 m²/g and a pore volume of 1.5 cm³/g was prepared as described in Example 11 and treated with vapours of vanadium chloride in an amount of 1.01 g. The resulting catalyst was set under vacuum at a temperature of 80°C. Analysis showed that the content of vanadium chloride was 47% by weight and that of the carrier was 53% by weight. The catalyst was in the form of spherical granules.

Polymerization of ethylene

- 110 0.047 g of the catalyst with a particle size of from 0.25 to 0.5 mm, 0.036 g of Al(i-C₄H₉)₃ and 50 ml of n-heptane were charged into a reactor provided with a stirrer. Ethylene was admitted thereto at a temperature of 80°C and polymerization was conducted under a constant pressure of the monomer of 223 mm Hg. After 6 hours there were obtained 0.082 g of polyethylene with a particle size of from 0.75 to 2 mm in the form of spherical granules. The yield of the polymer was 0.012 kg per one gram of vanadium. The rate of polymerization was 6.6 g/g vanadium.hr.atm.

Example 16

Polymerization of butene

- 125 0.02 g of the catalyst prepared as in Example 15, with a particle size of from 0.25 to 0.5 mm, 0.042 g of triisobutylaluminium and 17 ml of n-heptane were charged into a dilatometer provided with a stirrer and 0.47 g of liquid α-butene were added thereto.

The dilatometer was placed in a thermostat at a temperature of 50°C. After 4 hours there were obtained 0.45 g of poly- α -butene with a particle size of from 1.5 to 2 mm in the form of spherical granules. The polymer yield was 0.45 kg per one gram of vanadium. The rate of polymerization was 41 g/g vanadium.hr.atm.

Example 17

10 Polymerization of ethylene

0.0188 g of the catalyst prepared in Example 11, with a particle size of from 0.001 to 0.03 mm, 0.011 g of triisobutylaluminium and 300 ml of n-heptane were charged into a reactor provided with a stirrer.

- 15 At a temperature of 80°C ethylene was admitted thereinto and polymerization was conducted under a constant pressure of ethylene of 223 mm Hg. After 25 hours there were obtained 39 g of polyethylene. The polymer yield was 20.4 kg per one gram of vanadium. The rate of polymerization was 2,780 g/g vanadium.hr.atm.

Example 18

Polymerization of 4-methylpentene-1

- 25 0.05 g of the catalyst produced in Example 5 was charged into a dry ampule, and 0.7 g of $(C_2H_5)_2AlCl$ and 12.5 g of 4-methylpentene-1 were added. The ampule was sealed and placed in a thermostat at a temperature of 50°C. After 3.5 hours there were
- 30 obtained 0.2 g of poly-4-methylpentene-1. The polymer yield was 1.28 kg per gram of titanium.

Example 19

Copolymerization of ethylene and propylene

- 35 0.15 g of the catalyst prepared in Example 5, 0.5 g of $(i-C_4H_9)_2AlCl$ and 50 ml of n-heptane were charged into an apparatus provided with a stirrer. A mixture of ethylene with propylene was admitted into the reactor at a temperature of 70°C. After 4 hours,
- 40 methanol was added thereto. The precipitated copolymer was separated, dried and weighed. The yield of the copolymer of ethylene and propylene was 2.12 kg per one gram of titanium.

45 Example 20

Preparation of the catalyst

- 12.11 g of a carrier in the form of spherical granules and comprising a copolymer of 60% by weight of styrene and 40% by weight of divinylbenzene with a specific surface area of 360 m²/g and a pore volume of 1.42 cm³/g were treated with vapours of titanium chloride in a manner similar to that described in Example 9. The content of titanium chloride in the resulting catalyst was 48.5% by
- 50 weight. The catalyst was in the form of spherical granules.

Dimerization of ethylene

- 0.0967 g of the catalyst, 0.417 g of $(C_2H_5)_2AlCl$ 0.2
- 60 litres of benzene were placed in an autoclave provided with a stirrer. Dimerization was effected at a temperature of 80°C under a constant pressure of ethylene of 25 atm.g. After 2 hours, methanol was added to the reaction mixture. The resulting products were isolated and identified. The yield of

ethylene dimers was 32 g, of which 97% by weight was butene-1, and 3% by weight was cis-butene-2.

Example 21

70 Preparation of the catalyst

- 1.08 g of a carrier in the form of spherical granules and comprising a copolymer of 50% by weight of styrene, 20% by weight of methylmethacrylate and 30% by weight of divinylbenzene with a specific
- 75 surface area of 197 m²/g and a pore volume of 0.8 cm³/g were treated with vapours of titanium chloride in an amount of 0.14 g and $(C_2H_5)_2AlCl$ in an amount of 0.06 g in a manner similar to that described in Example 1. The resulting catalyst contained 2.5% by
- 80 weight of titanium chloride and was in the form of spherical granules.

Dimerization of ethylene

- 0.116 g of the catalyst, 0.417 g of $(C_2H_5)_2AlCl$ and
- 85 0.2 litres of benzene were charged into an autoclave provided with a stirrer. Dimerization was effected at a temperature of 20°C under a pressure of ethylene of 25 atm.g. for 2 hours. The yield of butene-1 was equal to 19 g which corresponds to 40% conversion
- 90 of ethylene.

Example 22

Preparation of the catalyst

- The catalyst was prepared following the procedure similar to that of Example 9. The carrier was a copolymer of 70% by weight of styrene and 30% by weight of methylmethacrylate with a specific surface area of 30 m²/g and a pore volume of 0.9 cm³/g in the form of irregularly-shaped granules. The content of titanium chloride was 5.6% by weight. The catalyst
- 95 was also in the form of irregularly-shaped granules.

Dimerization of ethylene

- Dimerization was effected following the procedure of Example 20. After 2 hours there were obtained 9.8
- 105 g of polyethylene and 533 g of butenes of the following composition: 63.8% by weight of butene-1; 21.7% by weight of cis-butene-2; 14.5% by weight of trans-butene-2. The yield of butenes per one gram
- 110 of titanium was 300 kg.

Example 23

Preparation of the catalyst

- 7.4 g of a carrier in the form of irregularly-shaped granules and comprising a copolymer of 40% by weight of styrene and 60% by weight of divinylbenzene with a specific surface area of 360 m²/g and a pore volume of 1.42 cm³/g were placed in a flask and treated with 6 g of $(C_2H_5)_2AlCl$. 0.4 g of the thus-
- 115 treated carrier was mixed with 0.8 g of the catalyst prepared as described in Example 9. The mixture was kept for 2 days at room temperature and then dried under a vacuum of 2.10⁻² mm Hg. The content of titanium chloride in the resulting catalyst was
- 125 38.7% by weight. The catalyst was in the form of irregularly-shaped granules.

Oligomerization of propylene

- 0.75 g of the catalyst, 1.4 g of $(C_2H_5)_2AlCl$ and 400 g
- 130 of propylene were charged into an autoclave pro-

vided with a stirrer. The process was conducted at a temperature of 70°C. After 4 hours there were obtained 14 g of oligomers of propylene.

5 Example 24

Preparation of the catalyst

4 g of a carrier with a particle size of from 0.2 to 0.7 mm in the form of spherical granules and comprising a copolymer of 50% by weight of styrene, 20% by weight of 4-vinylpyridine and 30% by weight of commercial divinylbenzene with a specific surface area of 176 m²/g and a pore volume of 1.2 cm³/g were treated with 0.8 g of titanium chloride and 25 g of (C₂H₅)₂AlCl in a manner similar to that described in Example 1. The content of titanium chloride in the thus-prepared catalyst was 6% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

20 0.4 g of the catalyst, 0.2 g of triethylaluminium and 130 g of propylene were charged into an autoclave provided with a stirrer. The process was conducted at a temperature of 70°C for two hours. The yield of polypropylene was 33 g; its particle size was 1.4 mm. 25 The product was in the form of spherical granules.

Example 25

Preparation of the catalyst

3.5 g of a carrier with a particle size of from 0.035 to 0.08 mm in the form of spherical granules and comprising a copolymer of 70% by weight of styrene and 30% by weight of divinylbenzene with a specific surface area of 700 m²/g and a pore volume of 0.3 cm³/g were treated with 0.37 g of titanium chloride and 0.15 g of diethylaluminium chloride in a manner similar to that of Example 1. The resulting catalyst contained 7% by weight of titanium chloride and was in the form of spherical granules with a size of from 0.035 to 0.08 mm.

Oligomerization of propylene

0.14 g of the catalyst, 0.21 g of diethylaluminium chloride and 130 g of propylene were charged into an autoclave provided with a stirrer. Oligomerization was conducted at a temperature of 70°C for two hours. The yield of liquid oligomers of propylene was 5 g.

Example 26

Preparation of the catalyst

0.26 g of a carrier in the form of spherical granules and comprising a copolymer of 70% by weight of styrene and 30% by weight of divinylbenzene with a specific surface area of 260 m²/g and a pore volume of 1.5 cm³/g were kept under vacuum for 4 hours at a temperature of 80°C, cooled to room temperature and treated with vapours of vanadium chloride. The resulting catalyst was set under vacuum of 10⁻³ mm Hg at a temperature of 80°C. The content of vanadium chloride in the thus-prepared catalyst was 31.1% by weight. The catalyst was in the form of spherical granules.

Polymerization of alpha-butene

0.02 g of the catalyst, 0.042 g of triisobutylalumi-

nium, 17 ml of n-heptane and 0.47 g of liquid alpha-butene were charged into a dilatometer provided with a stirrer. The dilatometer was placed in a thermostat at a temperature of 50°C. After 4-hours polymerization there were obtained 0.45 g of poly-alpha-butene which corresponds to 225 g per gram of vanadium.

Example 27

Preparation of the catalyst

The catalyst was prepared in a manner similar to that of Example 26. The carrier was a copolymer of 40% by weight of styrene and 60% by weight of divinylbenzene with a specific surface area of 500 m²/g and a pore volume of 2.8 cm³/g in the form of spherically-shaped particles with a size of from 0.035 to 0.08 mm. The content of vanadium chloride in the thus-prepared catalyst was 10% by weight. The catalyst was in the form of spherical granules.

Polymerization of propylene

0.303 g of the catalyst, 0.05 g of isobutylaluminium and 50 ml of n-heptane were charged into a reactor provided with a stirrer. Propylene was admitted thereinto at a temperature of 60°C and polymerization was carried out under a constant pressure of propylene of 470 mm Hg. The polymerization time was 6 hours. The yield of polypropylene was 1.46 g. The product had the form of spherically-shaped granules with a size of from 0.15 to 0.35 mm. The rate of propylene polymerization was 40 g per one gram of vanadium.hr.atm.

CLAIMS

1. A catalyst for di, oligo-, co- and polymerization of vinyl monomers, comprising an active phase which is a compound of a transition metal of Group IV or V of the periodic system deposited onto a polymeric carrier comprising a macroporous copolymer of vinyl and divinyl monomers with a specific surface area of from 30 to 700 m²/g, and a cocatalyst which is an organo-aluminium compound.
2. A catalyst as claimed in Claim 1, wherein the said carrier has a pore volume of from 0.3 to 2.8 cm³/g.
3. A catalyst as claimed in Claim 1 or 2, wherein the said carrier is a copolymer of styrene and divinylbenzene.
4. A catalyst as claimed in Claim 1 or 2, wherein the said carrier is a copolymer of styrene and diisopropenylbenzene.
5. A catalyst as claimed in Claim 1 or 2, wherein the said carrier is a copolymer of styrene, divinylbenzene and methylmethacrylate.
6. A catalyst as claimed in Claim 1 or 2, wherein the said carrier is a copolymer of styrene, ethyldivinylbenzene and vinylpyridine.
7. A catalyst as claimed in any of Claims 1 to 6, which has a particle size of from 0.001 to 1 mm.
8. A catalyst as claimed in any of Claims 1 to 7, which has a granulated form.
9. A catalyst as claimed in any of Claims 1 to 8, which contains a compound of titanium or vanadium

as the active phase.

10. A catalyst as claimed in Claim 9, wherein the compound of titanium or vanadium is a chloride thereof.

5 11. A catalyst as claimed in any of Claims 1 to 10, wherein the content of the active phase is from 1 to 60% by weight.

12. A catalyst according to Claim 1, substantially as herein described in any of the foregoing Exam-
10 ples.

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